

## ABSORPTION SPECTRA OF THALLIUM HALIDES

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Plates XVIII A, B

**ABSTRACT** The absorption spectra of TlI, TlCl and TlBr have been investigated in the region  $\lambda 6500 - \lambda 2200$ . An examination of the new absorption photographs obtained for TlI in the present work, has led to an important modification in the analysis of the main system  $^1\Pi - ^1\Sigma^+$ , reported earlier in emission. The origin had to be located at  $\nu 26339.6$  instead of at  $\nu 25780.0$  and the vibrational quantum numbers  $v'$  and  $v''$  had to be increased by 11 and 13 units respectively. The revised vibrational constants are

$$\begin{array}{lll} \omega_e' = 93.4 & \omega_e'' = 123.5 \\ \nu_e = 26361.7 & x_e' \omega_e' = 0.10 & x_e'' \omega_e'' = 0.09 \end{array}$$

No systems of TlI attributable to the transitions  $^3O^+ - ^1\Sigma^+$  and  $^1\Pi - ^1\Sigma^+$  have been obtained in absorption.

The two systems of TlCl lying between  $\lambda 4200 - \lambda 3800$  and one for TlBr in the region around  $\lambda 3950$  reported in emission have not occurred in absorption.

## INTRODUCTION

In the previous investigation on the emission spectrum of thallium iodide, the author (T. Rao and K. Rao., 1949) referred to the possible existence of bands due to the electronic transition  $^1\Pi - ^1\Sigma^+$ . If at all they are excited, they are expected to occur in the ultraviolet. Under conditions of emission in a transformer or oscillator discharge, they were not obtained. As they might appear probably in absorption, experiments have been carried out to investigate this point. Incidentally the investigation is extended to cover the entire region in the case of thallium iodide and of the remaining halides of thallium as well. This work has led to a very important modification in the analysis of the main system of TlI itself, namely in the location of the origin of the system, which could not be very definitely identified from emission spectrum. The  $^1\Pi - ^1\Sigma^+$  transition itself could not be obtained even in absorption. In the present paper these results are described and a comparison is also made of the absorption spectra of all the thallium halides.

The existing results on the absorption spectra of thallium halides can be briefly summarised in the following table.

TABLE I

Molecule	Authors	Description	Region	Transition
TlF	Butkow & Boizova, Howell & Coulson.	A continuum	$\lambda 2200$	$^1\Pi - ^1\Sigma^+$
		A band system	around $\lambda 2200$	
	"	"	$\lambda\lambda 2800-2600$	$^3\Pi^+ - ^1\Sigma^+$
		"	$\lambda\lambda 3300-2800$	
TlCl	Butkow, H & C	"	$\lambda\lambda 3400-3200$	$^3\Pi - ^1\Sigma^+$
		A continuum	$\lambda\lambda 2545-2475$	
	"	"	$\lambda 3106$	
		"	$\lambda 2890$	
TlBr	Butkow, H & C	A band system	$\lambda\lambda 3600-3400$	$^3\Pi - ^1\Sigma^+$
		A continuum	$\lambda 3330$	
TlI	Butkow	Diffuse bands	$\lambda\lambda 4200-3800$	

(H &amp; C—Howell and Coulson).

The foregoing table indicates clearly that while the study of the absorption spectra of the fluoride, chloride and bromide of thallium is sufficiently extensive, very little is known of the absorption of thallium iodide. For this molecule, the brief region  $\lambda 4200-\lambda 3800$  where 13 diffuse bands were recorded by Butkow is obviously a portion of that in which the extensive system in emission is described by the author in the earlier paper. In the present experiments, the entire region from  $\lambda 6500-2200$  is investigated for all the molecules.

## EXPERIMENTAL

The usual experimental arrangement is employed for the study of the absorption spectra.

*Source*:—The source of continuous spectrum from  $\lambda 6500-\lambda 2900$  is a special ultraviolet ribbon lamp constructed by the General Electric Company. The lamp has a special thin sucked-in window having a lens action and transmits down to  $\lambda 2900$ .

From  $\lambda 2900$  down to  $\lambda 2100$ , the source of continuous spectrum is the one described by Ramasastry (1948) consisting of an H. F. oscillator discharge through iodine vapour. This source has been found by us as very useful and simple in all experiments in absorption in the ultraviolet.

*Absorption tube*:—The absorption tube was of pyrex tubing 40 cm. long and 1 cm. in diameter open at both ends to avoid windows on which the substance might deposit itself. A circular diaphragm of the same diameter as the tube is held in position, at each end of the tube, to act as a

shield for extraneous light. These diaphragms are found very necessary to get good pictures. The substance is spread near the centre of the tube.

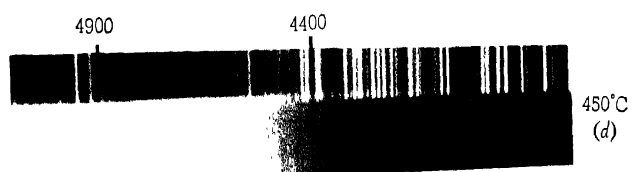
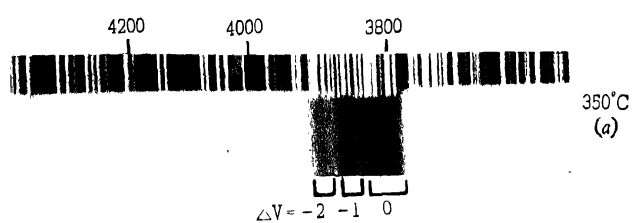
*Furnace* :—This is an electric furnace of hinged design, having units of helical coils of nichrome wire. It is of a very convenient design permitting inspection of the tube frequently. It is operated on 220 volts and 5 amperes. Any temperature up to  $600^{\circ}\text{C}$  can be easily obtained by regulating the current. The measurement of temperature is done by a standardised thermocouple supplied by the Cooley Electric Manufacturing Corp. (U.S.A.), The actual temperature range in which the absorption was studied in these molecules, extended from  $350^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ . This range was found suitable for the complete development of the absorption spectra.

*Instruments* :—Hilger medium quartz and a Fuess glass instrument were mainly used. For thallium iodide, the Fuess spectrograph was more suitable. Exposures were of 5 to 10 minutes' duration, on Ilford Special Rapid Panchromatic plates.

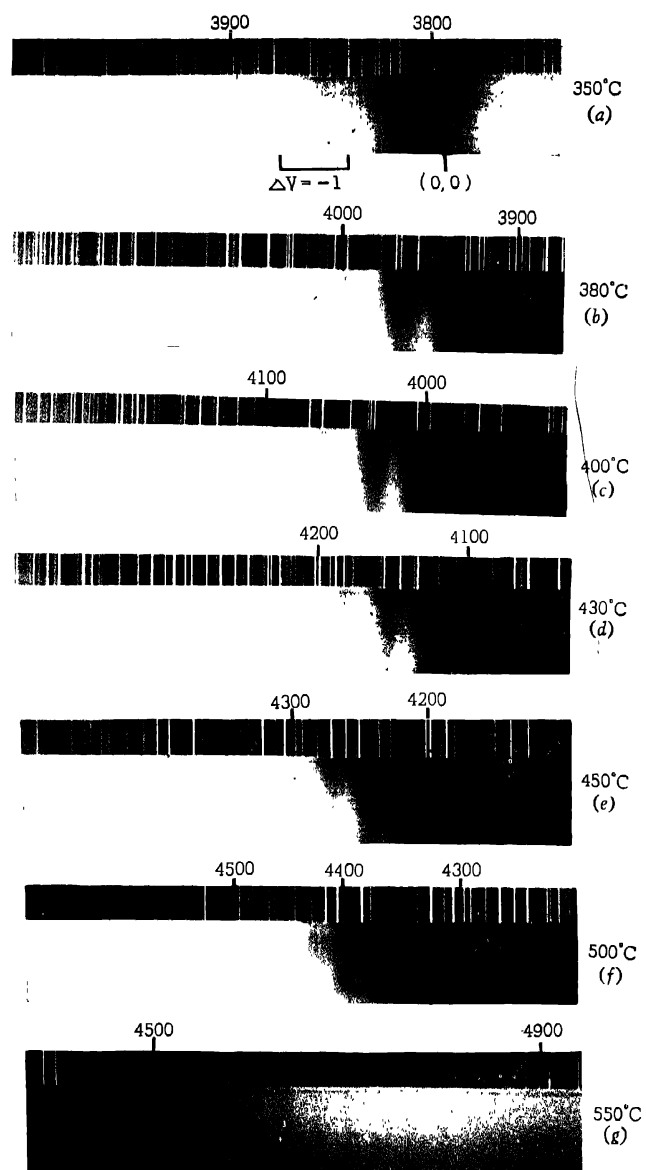
#### RESULTS

*Tl I* :—Plate XVIII A and strips (a) to (d) show the absorption spectra of thallium iodide at various temperatures taken on the medium quartz spectrograph. At  $350^{\circ}\text{C}$  four discrete groups of bands at about  $\lambda 3800$  and upwards, appear, the one in the extreme violet end being the strongest. The intensity of these groups decreases as we go towards longer wave-lengths. Some of these groups show banded structure which is partially resolved. This at once indicated the need for taking the picture on a higher dispersion instrument. At  $380^{\circ}\text{C}$  absorption extends to longer wave-lengths to about  $\lambda 4100$  while between  $\lambda 3950 - \lambda 3960$  there is complete absorption in the place of discrete bands. At  $400^{\circ}\text{C}$  absorption extends up to  $\lambda 4500$ . As the temperature increases, the shorter wave edge of absorption extends down to  $\lambda 3700$ .

Plate XVIII B strips (a) to (g) show the complete absorption spectrum of thallium iodide at various temperatures taken on the Fuess glass instrument of higher dispersion. At  $350^{\circ}\text{C}$ , the groups recorded previously on medium quartz instrument around  $\lambda 3800$  appear well resolved into discrete bands. This is just the region of the spectrum which is obscured partly by the intense Tl 3775 line, in emission. This picture proved to be of utmost importance in the location of the origin of the system. At higher temperatures as well, photographs with this instrument show well resolved discrete structure in places where just diffuse bands are found under the smaller dispersion of the quartz instrument. The extension of the spectrum towards longer wave-length side with increasing temperature may be clearly seen in the absorption photographs shown in Plate XVIII B strips (a) to (g). It is seen that at the highest temperature  $550^{\circ}\text{C}$ , the bands become exceedingly diffuse and extend up to  $\lambda 4700$ , which may be assumed to be the longer wave length



Til absorption spectra at various temperatures  
( medium quartz spectrograms )



TII absorption spectra at various temperatures  
( Fues spectrograms )

### *Absorption Spectra of Thallium Halides*

limit of the band system. At about the same temperature, the absorption bands of iodine are also recorded above  $\lambda 5000$ , probably because of the presence of free iodine formed as a product of thermal dissociation. These absorption photographs of thallium iodide, obtained so clearly for the first time in the present work, proved very useful in arriving at a definite analysis of the main system.

The second system of Tl I observed in emission and analysed as  $^2\text{O}^+ - ^1\Sigma^+$  is not obtained in absorption.

#### ANALYSIS OF Tl BANDS

In arriving at the analysis of the main system of this molecule from a study of the emission photographs, reference was made to one main difficulty in obtaining the starting point. The origin of the system had to be located at the violet end of the observed bands mainly from a consideration of analogy with the other thallium halides. The absorption photographs have clearly confirmed this view, for, both in emission and in absorption the violet limit is about  $\lambda 3800$ . The red end limit is at about  $\lambda 4700$  in absorption while it extends further to the red in emission. With increasing temperature, a gradual extension of the spectrum is observed in absorption towards the region of longer wave-lengths. Further the intensity of absorption is maximum in the most refrangible part of the spectrum.

The difficulty in exactly locating the origin from the emission photographs only, as was previously stated, is partly because this end is obscured by the intense Tl 3775 line. In this respect, the absorption spectrum has proved more useful. A close examination of these spectra has indicated that the origin of the system lies further to the violet than that located previously. The existence of well-defined and more prominent bands in the region  $\lambda 3795 - \lambda 3813$  necessitated this change. A re-assignment of the vibrational quantum numbers based on the shift in the origin of the system had to be made, adopting the very strong bands between  $\lambda 3795.49$  to  $\lambda 3838.59$  as the  $\Delta v = 0$  sequence. Table II gives the new assignments derived from the absorption pictures. Only the most refrangible portion of the bands below  $\lambda 3896.56$  are shown in this table. The wave-length and wavenumber data of the remaining bands are those given already in the previous paper. But the vibrational numbering should be changed consistently with the new numbering shown in Table II. It implies that for all the bands with wavenumbers below  $\nu = 25780.0$  cm. (which is assigned as the 0,0 band previously), the values of the vibrational quantum numbers  $v'$ ,  $v''$  should be increased by 11 and 13 respectively.

In the light of this new  $v'$ ,  $v''$  numbering, the constants of the system are re-calculated. There is obviously an alteration chiefly in the value of  $v_0$ , the remaining constants being almost identical on account of the very

TABLE II

TII Bands ( $\lambda 3790$ - $\lambda 3900$ )

Wave-length	Int	Wavenumber (Abs.)	Wavenumber (emission) data	Classification	
				Abs. ( $\nu'$ , $\nu''$ ) Revised	emis. ( $\nu'$ , $\nu''$ )
3795.49	10	26339.6	..	0,0	..
39.53	10	26311.6	...	1,1	...
3804.22	10	26279.2	..	2,2	..
08.59	10	26249.1	..	3,3	...
13.18	10	26217.4	26218.9	4,4	5,0
17.56	9	26187.3	26187.6	5,5	6,1
21.76	8	26158.6	26159.4	6,6	7,2
26.06	6	26129.5	26132.3	7,7	4,0
30.52	6	26098.7	26102.6	8,8	5,1
34.42	6	26072.2	26071.0	9,9	6,2
38.59	6	26043.9	26043.8	10,10	3,0
43.13	6	26013.1	26014.7	7,8	4,1
47.52	6	25983.4	25984.2	8,9	5,2
52.42	6	25950.4	25953.9	9,10	2,0
56.87	6	25920.5	25921.9	10,11	3,1
3861.32	6	25890.6	25890.0	11,12	4,2
65.78	5	25860.7	25863.8	12,13	1,0
69.76	5	25834.1	25836.3	13,14	2,1
74.15	5	25804.8	25807.5	14,15	3,2
78.41	4	25776.5	25780.0	11,13	0,0
82.69	5	25748.1	25750.8	12,14	1,1
87.29	4	25717.6		13,15	
96.56	4	25686.4	25684.8	14,16	0,1

TABLE III

Molecule	Approximate interval separations
TlF	1682
TlF I	1106*
TlBr	872*
Tl I	710

small magnitude of the anharmonic constants. These new values are given below (for comparison, the old values are also quoted in the foot note).\*

$$\nu_e = 26361.7 \quad \omega'_e = 93.4 \quad \omega''_e = 123.5 \quad x'_e \omega'_e = 0.10 \quad x''_e \omega''_e = 0.09$$

The interval separations between the origins of the two systems  $^3\Sigma^+ - ^1\Sigma^+$  and  $^3\Sigma^+ - ^1\Sigma^+$ , is also altered on account of the change in the value of  $\nu_e$ .

Table III gives the new value for Tl I along with those of the corresponding ones for the other thallium halides.

$$\nu_e = 25794.7 \quad \omega'_e = 91.2 \quad \omega''_e = 121.2 \quad x'_e \omega'_e = 0.10 \quad x''_e \omega''_e = 0.09$$

\* Values determined approximately from continua occurring on the shorter wave side of the main system.

ABSORPTION SPECTRA OF OTHER  
HALIDES OF THALLIUM

TlF : The absorption spectrum for this molecule is not taken as it has been thoroughly investigated previously by Howell

TlCl :—For this molecule the author recorded two new systems of bands in emission, the analyses of which have already been reported in a previous paper (T. Rao, 1949). It has been shown that these two systems occurring in the region  $\lambda_{4200}$ – $\lambda_{3800}$  have a common lower state which is the same as the upper state of the ultraviolet system around  $\lambda_{3200}$  analysed by Howell and Coulson. The author suggested that it is improbable to expect these systems in absorption as the ground state is not involved in the emission of the systems. This study of the absorption spectrum of TlCl was undertaken primarily to see whether these systems can be actually observed in absorption. No such systems are observed in the neighbourhood of  $\lambda_{3800}$  and  $\lambda_{4200}$ . For the sake of completeness, the absorption spectra of the system occurring around  $\lambda_{3200}$  were taken at various temperatures.

Both Butkow and Howell and Coulson observed a continuum at 3100 at about 200°C, while at about 450°C, Howell and Coulson recorded another continuum at  $\lambda_{2890}$ . In the present work, the continuum around  $\lambda_{3106}$  consists actually of two discrete continua, one with maximum at  $\lambda_{3110}$  and the other  $\lambda_{3160}$ . Further, both Butkow and Howell and Coulson recorded the spectrum up to  $\lambda_{3400}$  while in the present work, the spectrum extends up to  $\lambda_{3500}$ . As these additional bands have already been obtained in emission and analysed by Howell and Coulson, no quantitative data are given here. The ultraviolet absorption of TlCl around  $\lambda_{2520}$  has also been recorded.

TlBr :—For this molecule, Howell and Coulson (1938) reported a brief system around  $\lambda_{3950}$  as occurring only in emission, the lower state of which is found to be the upper state of the main system in the region  $\lambda_{3400}$ – $\lambda_{4500}$ . A revised analysis of this system is already given in a previous paper by the author. That the brief system occurs only in emission has also been confirmed by the author's experiments on absorption.

A discussion of the electronic transitions and the interpretation of the different band systems has already been given in the previous paper. The absorption experiments detailed above confirm that the lower state of the main systems in all these molecules is the ground state.

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